



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Eric WALTHER

Confirmation No.: 4096

Patent No.: 6,995,291 B2

Application No.: 10/668,790

Patent Date: February 7, 2006

Filing Date: September 22, 2003

For: PROCESS FOR THE OXIDATION OF  
UNSATURATED ALCOHOLS

Attorney Docket No.: 81455-5620

**REQUEST FOR CERTIFICATE OF CORRECTION  
UNDER 37 C.F.R. §§ 1.322 AND 1.323**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**Certificate  
FEB 24 2006  
of Correction**

Sir:

Patentees hereby respectfully request the issuance of a Certificate of Correction in connection with the above-identified patent. The corrections are listed on the attached Form PTO-1050. The corrections requested are as follows:

Title Page:

Item (56) References Cited, Other Publications:

"Aneli et al." reference, change "Aneli" to -- Anelli --; change "Aldehydesor" to -- Aldehydes or --; and change "pp2659-2663" to -- pp 2559-2663 --.

"Dijksman et al" reference, change "cholorinated" to -- chlorinated --; and change "pp 271-271" to -- pp 271-272 --.

Delete the "Nooy et al." reference in its entirety as it is a duplicate of the "de Nooy et al." reference.

"deNooy et al." reference, change "deNooy" to -- de Nooy --; change "Nitroxyl" to -- Nitroxyl --; change "Sunthesis George" to -- Synthesis, Georg --; and change "PP 1153-1174" to -- pp 1153-1176 --.

The above changes are merely to correct errors of a clerical or typographical nature.

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DC:455532.1

Column 9

Line 2, change "(O.)" to -- (O•) --. Support for this change appears in application claim 3.

A fee of \$100 is believed to be due for this request. Please charge the required fees to Winston & Strawn LLP Deposit Account No. 50-1814. Please issue a Certificate of Correction in due course.

Respectfully submitted,

Date

2-17-06

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212-294-3311

**UNITED STATES PATENT AND TRADEMARK OFFICE  
CERTIFICATE OF CORRECTION**

PATENT NO.: 6,995,291 B2  
DATED: February 7, 2006  
INVENTORS: Walther

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

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Line 2, change "(O.)" to -- (O•) --. Support for this change appears in application claim 3.



US006995291B2

(12) **United States Patent**  
**Walther**

(10) **Patent No.:** **US 6,995,291 B2**  
(45) **Date of Patent:** **Feb. 7, 2006**

(54) **PROCESS FOR THE OXIDATION OF**  
**UNSATURATED ALCOHOLS**

(75) **Inventor:** **Eric Walther, Geneva (CH)**

(73) **Assignee:** **Firmenich SA, Geneva (CH)**

(\*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 142 days.

(21) **Appl. No.:** **10/668,790**

(22) **Filed:** **Sep. 22, 2003**

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US 2004/0064000 A1 Apr. 1, 2004

**Related U.S. Application Data**

(63) Continuation of application No. PCT/IB03/00139, filed on Jan. 15, 2003.

(30) **Foreign Application Priority Data**

Jan. 29, 2002 (WO) ..... PCT/IB02/00304

(51) **Int. Cl.**  
**C07C 45/00** (2006.01)

(52) **U.S. Cl.** ..... **568/361; 568/363; 568/364;**  
**568/377; 568/403; 568/407; 568/408; 568/446;**  
**568/447; 568/471; 568/476**

(58) **Field of Classification Search** ..... **568/361,**  
**568/363, 364, 377, 403, 407, 408, 446, 447,**  
**568/471, 476**

See application file for complete search history.

(56) **References Cited**

**FOREIGN PATENT DOCUMENTS**

EP 1 103 537 A1 5/2001

**OTHER PUBLICATIONS**

Anelli et al., XP-002238208, "Fast and Selective Oxidation of Primary alcohols to Aldehydes or to Carboxylic Acids and of Secondary Alcohols to Ketones Mediated by Oxonium Salts under Two-Phase Conditions", Journal of Org. Chem, vol. 52, No. 12, pp2659-2663, (1987). pp 2559-2663  
Dijksman et al., XP-002238182, "Polymer immobilised TEMPO (PIPO): an efficient catalyst for the chlorinated hydrocarbon solvent-free and bromide-free oxidation of alcohols with hypochlorite". Chem. Commun. pp 271-271 pp 271-272 (2000).

~~Nooy et al., XP-002072173, "On the Use of Stable Organic Nitroxyl Radicals for the Oxidation of Primary and Secondary Alcohols," Synthesis, Georg Thieme Verlag, Stuttgart, DE, PP 1153-1174 (1996).~~

deNooy et al., XP002072173, "On the Use of Stable Organic Nitroxyl Radicals for the Oxidation of Primary and Secondary Alcohols," Synthesis Georg Thieme Verlag, Stuttgart, DE, pp 1153-1174 (1996). de Nooy Nitroxyl Synthesis, Georg pp 1153-1176  
C. Bolm et al., "TEMPO Oxidations with a Silica-Supported Catalyst," Chem. Commun., 1999, pp. 1795-1796.

*Primary Examiner*—Sikarl A. Witherspoon

(74) *Attorney, Agent, or Firm*—Winston & Strawn LLP

(57) **ABSTRACT**

The present invention relates to the field of organic synthesis and more precisely to a process for the synthesis of an unsaturated aldehyde or ketone by oxidation of the corresponding alcohol. The oxidation is performed by a hypochlorite salt and a catalytic amount of a N-(2,2,6,6-tetraalkyl-4-piperidiny-N-oxyl)-2-amino-1,3,5-triazine compound, preferably a N-oxyl derivative of one of the polymers known under the trademark Chimassorb® 944 or 2020.

**14 Claims, No Drawings**

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(O•)

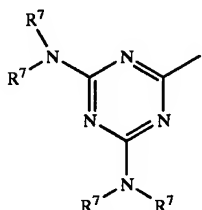
$R^3$  represents, simultaneously or independently, a hydrogen atom or an oxyl radical (O•), with the proviso that at least one  $R^3$  group is an oxyl radical;

X represents an oxygen atom or a  $-NR^4$ -group;

$R^4$  represents, simultaneously or independently, a hydrogen atom, a 2,2,6,6-tetramethyl-4-piperidiny group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group or a  $C_1$  to  $C_{15}$  linear, branched or cyclic saturated or unsaturated hydrocarbon group, said hydrocarbon group optionally including one or two oxygen or nitrogen atoms; or two  $R^4$  groups, bonded to the same nitrogen atom, may be bonded together to form a heterocycle having 5 to 7 members and which may contain an oxygen atom;

$R^5$  represents, simultaneously or independently, a hydrogen atom or a  $NR^6_2$  group;

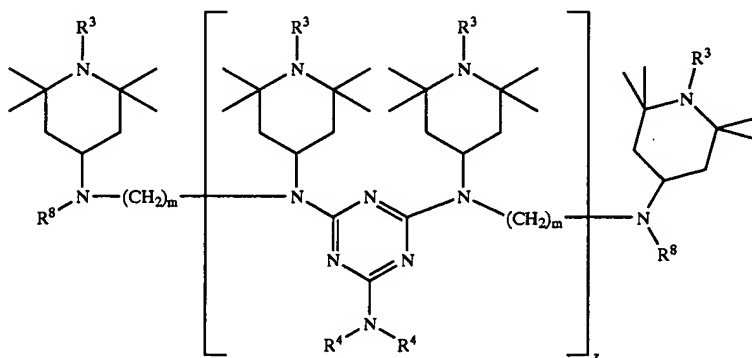
$R^6$  represents, simultaneously or independently, a hydrogen atom, a  $C_1$  to  $C_{20}$  linear, branched or cyclic saturated or unsaturated hydrocarbon group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group, a 2,2,6,6-tetramethyl-4-piperidiny group or a group of formula



$R^7$  representing, simultaneously or independently, a hydrogen atom, a  $C_1$  to  $C_{12}$  linear or branched alkyl group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group or a 2,2,6,6-tetramethyl-4-piperidiny group; and

Y represents, simultaneously or independently, a  $C_2$  to  $C_{20}$  linear, branched or cyclic alkylene group optionally including one or two oxygen or nitrogen atoms.

4. The process of claim 3, wherein the N-(2,2,6,6-tetraalkyl-4-piperidiny-N-oxyl)-2-amino-1,3,5-triazine compound is a polymeric or oligomeric compound of formula



wherein  $z$  represents an integer from 2 to 10;

$m$  represents an integer from 2 to 12;

$R^3$  is as defined in claim 3;

$R^4$  represents, simultaneously or independently, a hydrogen atom, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl

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radical group, a 2,2,6,6-tetramethyl-4-piperidiny group or a  $C_1$  to  $C_{10}$  linear or branched alkyl or alkenyl group; or two  $R^4$  groups, bonded to the same nitrogen atom, may be bonded together to form a heterocycle having 6 members and which may contain an oxygen atom; and

$R^8$  represents, simultaneously or independently, a hydrogen atom, a  $C_1$  to  $C_{10}$  linear or branched alkyl or alkenyl group, a 2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical group, a 2,2,6,6-tetramethyl-4-piperidiny group or a group of formula (V).

5. The process of claim 4, wherein the N-(2,2,6,6-tetraalkyl-4-piperidiny-N-oxyl)-2-amino-1,3,5-triazine derivative is a N-oxyl derivative of the polymers having the CAS Registry Numbers 71878-19-8 or 192268-64-7.

6. The process of claim 1, wherein the hypochlorite salt is selected from the group consisting of NaOCl, KOCl and  $Ca(OCl)_2$ .

7. The process of claim 1, wherein one of a bromide salt of formula  $M'Br$  or a bicarbonate of formula  $M'HCO_3$  is added to the process, wherein  $M'$  is an alkaline metal.

8. The process of claim 1, wherein a bromide salt of KBr or NaBr is added to the process.

9. The process of claim 1, wherein a bicarbonate of  $KHCO_3$  or  $NaHCO_3$  is added to the process.

10. The process of claim 1, wherein the catalyst has a concentration ranging from 0.02 to 0.15 molar equivalents relative to the amount of alcohol.

11. The process of claim 1, wherein the hypochlorite salt is added to the reaction mixture in an amount of between 0.9 and 2.5 molar equivalents relative to the amount of alcohol.

12. The process of claim 1, which is carried out at a temperature ranging between  $0^\circ C.$  and  $60^\circ C.$

13. The process of claim 1, conducted in a solvent.

14. The process of claim 1, conducted in the absence of a solvent.

\* \* \* \* \*